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LIMESTONE AND DOLOMITE IN THE CHEMICAL AND PROCESSING INDUSTRIES

BY

OLIVER BOWLES AND MABEL S. JENSEN

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LIMESTONE AND DOLOMITE IN THE CHEMICAL AND PROCESSING INDUSTRIES[1/]

By Oliver Bowles[2/] and Mabel S. Jensen[3/]

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WIDE APPLICATION OF LIMESTONE

When, as in the present national defense emergency, many industries are striving to attain maximum production, it is pertinent to review the output, uses, and requisite qualities of limestone, which is employed as an essential raw material in innumerable processes and products. Because of its ready availability and the multitude of uses for which it is employed, production of limestone exceeds that of any other rock. In 1939 limestone sold or used in the United States (including that employed in cement and lime manufacture) exceeded 139,000,000 tons or about 75 percent of the quantity of all kinds of stone sold or used during that year. Limestone was quarried in every State except Delaware, the District of Columbia, and New Hampshire. Although the major consumption of limestone is in the form of concrete aggregate, road material and railroad ballast, or as a fluxing stone in blast furnaces, for cement and lime manufacture, as agricultural limestone, as riprap for shore protection, for harbor work and spillways

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at dams, and as building stone, approximately 25,000,000 tons or approximately 35 percent of the total commercial limestone handled annually is consumed by the manufacturing and chemical industries which play an important part in our defense program, and with which this paper is chiefly concerned. To this quantity must be added considerable tonnages of burned lime, which is essential to many processes. For many of these uses the percentage of impurity in the stone must be low. Although the quantities used by some industries may be relatively small they perform useful and essential functions for which it is difficult if not impossible to find substitute materials.

COMPOSITION

Limestone, a sedimentary rock of wide occurrence in nature, consists essentially of calcium carbonate or of a mixture of the carbonates of calcium and magnesium. When 10 percent or more of magnesium carbonate is present the rock is termed "magnesium" or "dolomitic" limestone; if the amount approaches 45 percent the rock is composed essentially of the double carbonate of lime and magnesium ($CaCO_3$).($MgCO_3$), the mineral dolomite. The principal impurities in limestone are sand, clay, and iron oxide. Marble is similar in composition and can be used in the same processes as limestone.

STATISTICAL HISTORY OF PRINCIPAL CHEMICAL AND PROCESSING USES

The largest consumers of limestone for chemical or processing uses are the following industries:

Alkali	Paper
Asphalt (filler)	Refractory-stone (dead-burned dolomite)
Calcium carbide	Sugar
Glass	Whiting
Metallurgical (flux)	
Mineral (rock) wool	

Each of the above-mentioned industries consumes 120,000 to over 17 million short tons of limestone annually. In these industries, with the exception of mineral wool, lime (burned limestone) as well as raw stone is used. The sales of raw stone for the above purposes amounted to 24,757,420 short tons in 1939, but the figure is increased to approximately 29 million short tons if stone burned and sold as lime is included.

Fertilizer filler, filter beds, magnesia works, and mineral food industries consume smaller quantities of limestone and dolomite but nevertheless have considerable importance.

The following tables furnish a historical summary of the quantity and value of limestone (exclusive of lime) used in 10 of the larger limestone-consuming industries from 1920 through 1939, and the quantity and value of burned lime sold to 5 of them. The chart (fig. 1) is a graphic presentation of trends in the four major uses for the 20-year period, 1920-39. Figure 2 shows graphically total sales of limestone and dolomite to the chemical and processing industries in 1939, by uses:

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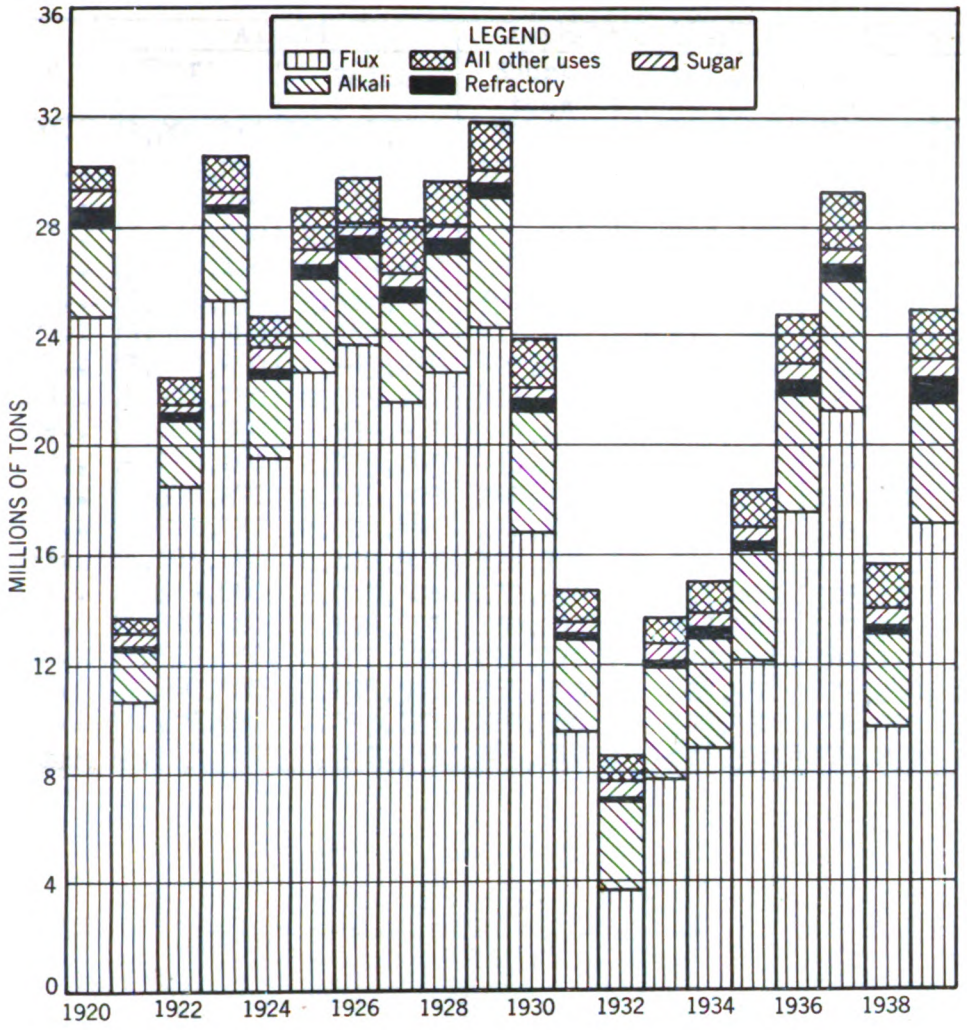

Figure 1.—Quantity of limestone (exclusive of lime) sold or used for the principal chemical and processing industries, 1920-39.

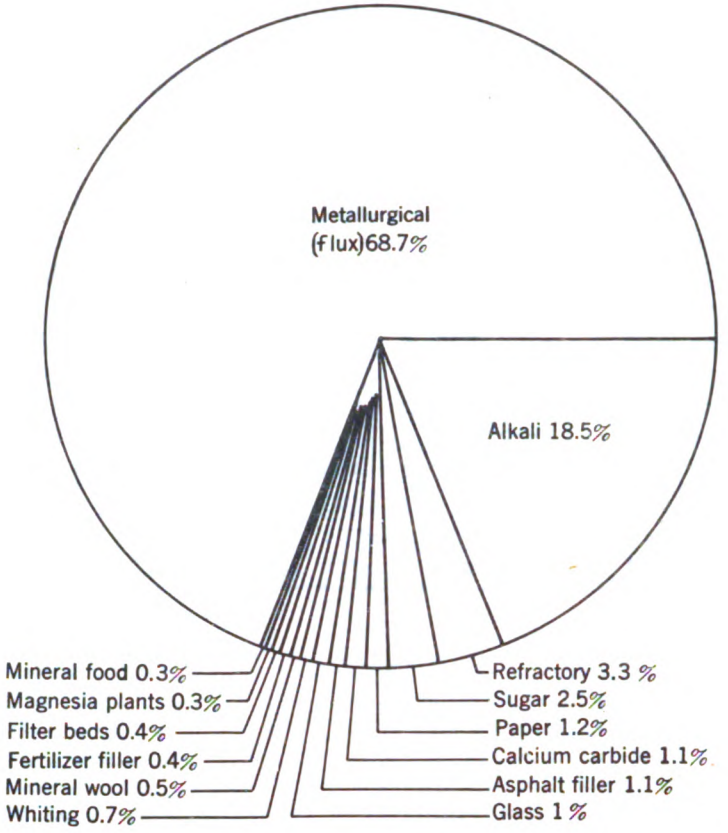

Figure 2.—Quantity of limestone and dolomite sold to the chemical and processing industries in 1939, by uses.

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Quantity and value of limestone sold or used in the principal chemical and processing industries, 1920-39

Year	Alkali		Asphalt filler		Calcium carbide		Glass		Metallurgical (flux)	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1920..	3,205,160	$2,229,680	71,970	$309,075	265,174	$173,736	196,150	$400,873	24,977,190	$26,475,763
1921..	1,738,280	1,465,580	128,120	532,621	227,260	129,641	118,970	232,715	10,044,290	9,428,767
1922..	2,494,260	1,878,702	138,930	549,281	256,190	117,939	166,070	291,854	18,690,270	14,208,457
1923..	3,333,910	2,348,223	225,400	728,386	276,760	138,854	197,380	301,403	25,562,140	20,333,939
1924..	2,950,120	2,074,509	284,850	1,052,427	312,670	153,572	177,260	286,164	19,683,150	15,827,464
1925..	3,549,930	2,486,883	390,140	1,399,574	308,660	203,506	324,160	412,832	22,840,500	17,318,366
1926..	3,556,490	2,354,040	415,920	1,415,352	357,450	234,889	326,280	543,163	23,849,700	18,021,449
1927..	3,848,490	2,449,284	420,860	1,343,987	316,960	164,875	247,210	420,415	21,660,820	15,977,484
1928..	4,231,750	2,585,216	407,350	1,284,983	282,610	178,902	281,260	441,906	23,094,090	16,929,986
1929..	5,004,930	3,234,457	344,880	1,165,538	339,510	236,412	257,370	455,367	24,337,280	17,994,110
1930..	4,436,160	2,759,245	430,290	1,122,939	364,750	275,296	224,180	349,771	17,021,350	12,312,602
1931..	3,340,290	2,186,422	247,450	778,045	164,180	96,158	159,220	244,466	9,674,800	7,160,630
1932..	3,211,770	2,084,444	177,110	450,530	138,050	125,430	108,720	149,262	3,945,170	2,902,847
1933..	4,193,650	2,120,908	126,780	332,159	117,740	75,077	199,720	245,835	7,982,560	5,510,445
1934..	3,814,060	2,015,506	172,170	361,404	305,600	177,458	161,220	260,410	9,230,880	6,297,579
1935..	4,090,980	2,188,597	152,040	363,163	287,340	135,844	250,930	414,027	12,191,660	7,902,717
1936..	4,394,670	2,107,012	210,370	498,031	348,170	178,694	265,890	429,546	17,724,880	11,576,156
1937..	4,860,520	2,295,599	351,590	686,951	472,240	266,557	274,770	460,352	21,311,250	14,685,215
1938..	3,634,050	1,743,173	288,590	789,587	246,010	137,522	170,560	290,297	9,692,130	6,933,621
1939..	4,655,960	2,100,535	265,710	676,978	274,890	233,085	240,840	394,727	17,271,560	12,618,938

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Quantity and value of limestone sold or used in the principal chemical and processing industries, 1920-39 (Cont'd

	Mineral wool[1]		Paper		Refractory		Sugar		Limestone whiting	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1920..	21,570	$24,773	139,880	$256,278	612,800	$742,020	637,090	$1,200,394	60,890	$499,540
1921..	(2/)	(2/)	120,460	223,601	79,480	85,786	570,840	1,019,288	29,560	264,244
1922..	9,170	10,622	149,430	264,130	146,640	172,251	371,430	634,511	66,200	405,783
1923..	6,940	9,333	206,740	326,054	205,890	249,993	474,530	875,774	81,310	514,258
1924..	7,530	14,808	138,280	236,834	309,010	287,137	618,230	1,055,505	66,910	417,326
1925..	12,660	14,308	109,730	198,691	415,710	375,315	471,580	796,974	82,290	511,406
1926..	18,830	19,448	202,460	319,998	511,300	458,802	416,920	771,488	95,650	549,139
1927..	15,390	12,962	289,010	436,204	434,160	424,140	483,800	881,370	124,840	551,915
1928..	31,700	27,042	155,050	290,590	522,850	509,502	487,060	851,850	95,400	442,742
1929..	83,920	92,092	273,880	456,251	516,400	461,444	487,990	874,909	125,430	626,692
1930..	64,850	70,988	248,790	377,059	453,350	356,025	414,340	733,359	119,350	492,894
1931..	73,640	67,393	194,310	288,143	263,500	183,020	453,640	748,682	73,420	408,880
1932..	43,180	38,321	152,710	231,618	72,240	45,186	507,980	772,587	76,020	386,191
1933..	55,160	42,305	196,440	285,850	196,540	180,160	607,990	887,630	93,070	481,677
1934..	68,820	54,087	262,160	408,022	300,180	287,030	479,900	658,502	97,340	509,893
1935..	96,940	81,905	188,090	339,372	321,860	265,506	460,460	640,375	147,910	563,514
1936..	180,320	151,932	255,880	399,861	401,320	391,561	540,470	754,967	179,110	894,913
1937..	146,330	116,084	322,810	589,091	576,900	580,720	566,620	862,660	194,080	923,494
1938..	86,400	85,378	223,450	373,207	263,930	274,624	619,910	878,028	145,170	671,842
1939..	123,720	102,670	302,620	438,097	824,930	713,991	621,730	853,235	175,460	948,528

1/ The tonnages of limestone for mineral wool recorded herein include only the quantities sold to mineral wool companies, or used by companies that manufacture mineral wool as a subsidiary to a lime, cement, or other limestone product industry. The total limestone slag and shale used in 1939 in mineral-wool production is estimated at about 600,000 tons.

2/ Figures not available.

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Quantity and value of lime sold or used in the principal chemical and processing industries, 1920-39

Year	Calcium carbide		Dead-burned dolomite		Glass		Metallurgical		Paper	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1920..	88,465	$801,882	316,293	$3,732,522	54,747	$551,945	344,921	$2,836,474	365,897	$3,844,084
1921..	19,597	173,849	107,664	1,113,010	43,851	367,796	164,245	1,232,748	235,855	2,207,938
1922..	(1/)	(1/)	348,838	2,813,946	62,187	463,628	200,799	1,458,553	310,229	2,683,487
1923..	5,513	51,709	357,642	3,599,116	78,942	676,291	373,020	3,044,383	311,309	2,768,909
1924..	14,921	140,196	328,659	3,209,257	72,822	622,456	336,813	2,727,518	300,101	2,528,242
1925..	16,354	140,000	392,147	3,730,510	73,011	628,909	411,190	3,007,228	376,670	3,174,851
1926..	22,285	177,100	386,715	3,593,731	84,263	713,321	408,234	2,860,338	423,322	3,492,996
1927..	27,037	188,613	374,415	3,459,803	78,994	665,026	406,063	2,640,658	429,606	3,413,030
1928..	32,596	194,334	448,761	4,283,036	76,161	588,305	504,248	3,055,081	429,334	3,260,733
1929..	30,999	183,388	488,032	4,261,942	75,283	544,760	578,488	3,258,992	411,017	3,057,350
1930..	26,332	162,311	351,740	3,045,082	62,912	408,429	415,692	2,371,222	378,721	2,652,232
1931..	23,907	137,652	243,769	1,856,971	59,148	345,780	290,352	1,714,368	286,745	1,781,793
1932..	22,833	98,697	135,733	1,055,339	51,142	259,973	170,518	936,291	259,418	1,491,160
1933..	23,247	89,485	261,812	2,064,869	82,634	391,565	265,963	1,406,480	304,729	1,687,869
1934..	35,803	162,731	324,868	2,698,414	76,232	507,031	334,406	2,003,788	293,798	1,899,053
1935..	52,535	267,791	455,258	3,785,834	91,714	641,081	452,759	2,737,419	344,531	2,205,155
1936..	74,723	378,768	596,751	4,887,243	113,255	775,420	572,574	3,491,701	396,867	2,495,420
1937..	109,755	565,309	617,706	5,217,833	167,438	1,153,845	694,814	4,199,960	447,728	2,892,552
1938..	116,173	615,682	366,626	3,095,355	126,840	859,937	493,522	3,073,625	402,021	2,562,317
1939..	85,218	418,061	671,561	5,447,554	148,102	1,003,843	748,853	4,328,564	464,224	2,904,160

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MAJOR APPLICATIONS

Following is a brief discussion of the ways in which limestone and lime are used in manufacturing industries, the types of stone required, and the producing localities.

Alkali

In the manufacture of soda ash by the ammonia-soda process, about 1 1/4 tons of high-calcium limestone is used for each ton of soda ash produced. The stone is calcined at the chemical plant, and both the lime and carbon dioxide gas are used. Stone ranging from 1 to 6 inches in diameter is desired. Although the stone used should be as near chemically pure as possible to produce the best results, the average value received for limestone for use in alkali works has maintained a very low price compared with stone used in other chemical industries. The average value a short ton at the quarry has ranged between 45 and 84 cents for the past 20 years. The price has declined gradually since the peak year, 1921.

A large portion of the limestone produced for use in alkali works is captive tonnage; that is, it is produced by the industry that uses it. For a number of years, Michigan and New York were the only States producing high calcium stone for this use; but in 1939, 9 companies operating 12 plants reported tonnage from 6 States. Alpena, Presque Isle, and Wayne Counties, Mich., with a total output of 2,825,040 short tons in 1939, constitute the largest producing area in the United States. Other producing centers, according to rank of importance in output are: Oneida and Onondaga Counties, N. Y.; Winn Parish, La.; Smythe County., Va.; Bexar and Comal Counties, Tex.; and San Bernardino County, Calif. Only a very small tonnage of stone burned and sold as lime was reported for use in alkali manufacture in 1939.

A considerable quantity of the limestone employed in alkali manufacture is converted into a byproduct that is reused. The Michigan Alkali Co., Wyandotte, Mich., uses large quantities of limestone in making soda ash and caustic soda from common salt. In making soda ash the principal by-product is calcium chloride, largely a waste material; however, in making caustic soda from the soda ash, lime is used, and large quantities of calcium carbonate sludge are produced. Instead of recalcining this material to lime, as in the paper and beet-sugar industries, it is used for the manufacture of portland cement in an adjoining subsidiary plant.

Asphalt Filler

Pulverized limestone is useful as a filler in asphalt because it hardens the product, gives it stability, and renders it less affected by heat. Any kind of limestone may be used for this purpose, as composition and color are immaterial.

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The value a short ton of limestone for asphalt filler is considerably higher than that used in most of the other processing industries, owing to the fact that the stone must be finely pulverized (approximately 80 percent through a 200-mesh screen). Because this use of limestone is not confined to any certain areas and also because the content of the stone is unimportant, it has a wider range of producing localities than stone for the other industries discussed in this paper. Limestone for this use is a byproduct at many plants, but several companies now sell it as one of their principal products.

The largest producing States in 1939 were New York, Ohio, Virginia, Pennslyvania, Michigan, and Texas, in order of importance, with each reporting an output of over 20,000 tons a year. Fifteen other States reported production ranging from a few hundred to 11,000 tons. Forty-six companies operating a total of 52 plants reported sales in 1939.

Calcium Carbide

Calcium carbide and calcium cyanamide are products of the electric furnace. Calcium carbide is formed when a charge of lime and coke, mixed in the proportion of 60 and 40 percent, respectively, is heated to 2,000° C. Approximately 2 tons of limestone or 1 ton of lime is required for each ton of calcium carbide manufactured. Calcium cyanamide is derived from the carbide by treating it with nitrogen. Calcium carbide is important chiefly because, with water, it forms acetylene, used for lighting and for the steel-cutting and welding torch. One of the newer uses is in the manufacture of synthetic rubber. Calcium cyanamide is a nitrogenous fertilizer.

A very pure, high-calcium limestone must be employed in the manufacture of these products, especially if the carbide is to be used for acetylene. The limestone should contain little or no phosphates, for these form phosphides which, on burning, leave a white deposit. The stone also must be free from magnesium carbonate, for magnesium does not form a carbide, and the presence of its oxide in the charge makes the electrolytic process less efficient.

According to the Census of Manufactures six plants were producing calcium carbide in the United States in 1937, the latest year for which final data are available. Plant locations are as follows: Alabama 1; Iowa 2; Michigan 1; New York 1; Virginia 1. Seven plants are recorded for 1939, but the locations are not listed. In 1939 five limestone companies reported a production of 274,890 short tons of raw stone sold for the manufacture of calcium carbide, one in Presque Isle County, Mich.; two in Botetourt County, Va.; and one each in Carroll and Giles Counties, Va. Sales of burned lime for this use, amounting to 85,218 short tons in 1939, were reported from Indiana, Michigan, Missouri, Pennsylvania, Tennessee, and Virginia.

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Glass

In the manufacture of glass either lime or limestone of high calcium or high magnesium content may be used. High-calcium limestone is used in making bottle and window glass, whereas dolomitic stone is used for special glasses. Uniform stone must be used for each type of glass in order that the product may have constant chemical and physical properties. Common glass is made from the fused mixture of alkali, lime or limestone (limestone may constitute as much as 30 percent of some glass batches), and silica. Limestone for use in clear, colorless glass products must contain a very low percentage of iron oxide.

In 1939, 240,840 short tons of limestone and 148,102 tons of lime were sold to the glass industry of the United States. Converting the lime to its equivalent of limestone, the total stone used was approximately 537,000 short tons. Production of limestone for glass making was confined to 11 States, with Ohio, the leading State, reporting approximately 67 percent of the total output. Sales of Ohio lime to glass works amounted to 140,160 short tons and limestone to 81,630 short tons in 1939. Other leading States in the production of limestone for glass making were, in order of production: Missouri, Pennsylvania, Indiana, California, Arkansas, Illinois, and Michigan, with small tonnages reported from Texas, Tennessee, and Connecticut.

Metallurgical (Flux)

Enormous quantities of lime and limestone for use as fluxing material are consumed annually in blast furnaces and open hearth and electric steel plants and to a smaller degree in nonferrous metallurgy. Most iron ores carry alumina and silica as impurities, and the addition of a basic flux such as limestone is necessary to form a slag with them. The limestone also removes sulfur, which is an impurity in iron and steel. It is evident, therefore, that limestone, to be efficient as a flux, should be relatively free from alumina and silica. If more than small percentages of these elements are present, the stone is less effective, increases slag volume and fuel consumption, and slows production.

In 1939 stone for this purpose was reported from 30 States, and sales totaled over 17 million short tons or 17 percent of total limestone sold. The largest producing States were Michigan, with 31 percent of the total output; Pennsylvania, 30 percent; Ohio, 16 percent; West Virginia, 7 percent; and Alabama, 6 percent. Limestone used as flux comprised approximately half of the total limestone tonnage reported in the above States, with the exception of Ohio. Seventy-five percent of all flux sold was used in blast furnaces, 20 percent in open-hearth steel plants, and the remainder in copper, silver, aluminum, and lead smelters. Arizona, California, Montana, Nevada, Texas, Utah, and Washington are the only States where flux is sold to copper, silver, aluminum, and lead smelters. Flux from all the other States goes into iron and steel manufacture.

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Sales of burned lime for fluxing purposes amounted to over 700,000 short tons in 1939, and production was reported from 25 States. Pennsylvania contributed 23 percent of the total sales; West Virginia, 11; Missouri, 10; and Alabama, 9. Seventy-five percent of the total output was consumed in open-hearth and electric steel furnaces; 20 percent in ore concentration; and the smelting of nonferrous metals, wire drawing, mold paints, and foundry uses made up the remaining 5 percent.

Mineral wool

Mineral wool (also known as rock wool) was probably first made in Wales as early as 1840, where it was used as insulation for boilers and steam pipes, and in Germany shortly afterward for use as noninflammable material for Christmas tree decorations. It was introduced in this country in Cleveland, Ohio, in 1883, but commercial production did not begin until 1897, when a plant was constructed in Indiana. The greatest growth of the industry has taken place in the last 15 years, with a strong upturn in 1929 and a well-sustained output during the depression years when the demand for other building materials had dropped to a very low point.

There are three distinct types of mineral wool, as follows:

Rock wool - made from argillaceous limestones or mixtures of limestones, clays, and other rock substances.
Slag wool - made from furnace slag, alone or mixed with small quantities of other materials.
Glass wool - made from silica sand, soda ash, limestone, and other constituents of the glass batch.

This paper relates primarily to mineral wool manufactured from limestone.

Mineral wool is light, soft, and fibrous because it consists of flexible, interlaced filaments so fine that, individually, they are almost invisible to the naked eye and will float in the air. Suitable rock materials are melted in high-temperature furnaces; and as the molten mass leaves the furnace, a jet of high-pressure steam (or exceptionally compressed air) is directed against it, blowing the material into tiny molten beads which, by friction against the air, are elongated into fine threads.

Deposits of so-called "wool rock," such as are found in Indiana, which are suitable for manufacture into mineral wool without the addition of any considerable quantity of other material are not common. However, with the recent expansion of the industry, plants have been established in localities where the natural deposits are not suitable for use alone, and considerable blending with shale, silica sand, and other materials is necessary in order to obtain a cupola charge of the correct composition.

The Illinois Geological Survey[3/] has pointed out that an approximate and satisfactory method of estimating the suitability of any limestone for

3/ Lamar, J. E., Willman, H. B., Fryling, C. F., and Voskuil, W. H., Illinois State Geol. Survey Bull. 61, 1934, p. 15.

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mineral wool manufacture is to determine its loss on ignition, in other words, its CO_2 content. If, after being dried, a stone loses 20 to 30 percent of its weight being ignited, it probably will have definite possibilities for the making of mineral wool without the addition of other materials. If the loss of CO_2 is outside these limits, the stone is probably not suitable unless other materials are added.

The manufacture of mineral wool is a comparatively simple process, because it can be made without a great deal of technical knowledge. Production methods have been so improved that equipment producing 8 tons daily several years ago now produces 15 to 20 tons.

In the early stages of the industry in this country, mineral wool was used chiefly as an insulating material in refrigerators and fireless cookers, but today the principal use is in heat insulation and sound absorption. Mineral wool is ideally suited to both industrial and household insulation in that it is moisture proof, fire proof, and vermin proof.

During the past 20 years, modern methods of manufacturing mineral wool have taken it out of the luxury class and made it available to home owners in all income groups. Today, its fastest growing market is in the insulating of side walls and top floor ceilings of low-cost houses. Mineral wool has an outlet in building in insulating new homes as well as those that have already been built. It is claimed that a 4-inch thickness of mineral wool affords insulation equivalent to that of a 9-inch stone wall. There are also many less-important uses of this product.

For a number of years the only producing localities were near Yorktown, Delaware County, and Alexandria, Madison County, Ind. In 1939 mineral wool plants of all kinds are located as follows: California, 4 plants; Illinois, 8; Indiana, 19; Iowa, 1; Kansas, 2; Kentucky, 2; Massachusetts, 1; Michigan, 4; Minnesota, 1; Missouri, 3; New Jersey, 6; New York, 2; Ohio, 9; Oklahoma, 2; Pennsylvania, 7; Tennessee, 2; Texas, 5; Utah, 3; Virginia, 1; West Virginia, 1; and Wisconsin, 3. Production in 1939 is estimated at 500,000 tons, and the capacity is estimated at 600,000 tons.

The general trend at present seems to be toward decentralization of mineral wool plants to supply local demands more economically, as the large volume of a ton of mineral wool limits the quantity that can be loaded into a box car to approximately 12 tons, making freight rates high.

Paper

Both lime and limestone are used in the paper industry in the preparation of the cooking liquor. By digesting the wood with an acid liquor, all the constituents of the wood chips except cellulose are dissolved and removed. The cooking liquor is produced by the chemical reaction between sulfur dicxide and lime.

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For the milk-of-lime method of making sulfite pulp, a high-magnesium or dolomitic lime is preferred. However, if the Jennsen tower system is used, limestone rather than lime is employed, and a high-calcium stone generally gives better service than a high-magnesium stone.

For the soda pulp and sulfate pulp processes, a high-calcium lime containing less than 2 percent magnesia is desired. Lime having as much as 7 percent iron oxides, silica, and alumina has been used, but in general the purer the lime the better.

Limestone for use in the manufacture of chemical pulp was quarried in 24 States in 1939, and total production of stone (including that sold as lime) amounted to approximately 1,231,000 short tons. Washington ranks first in the production of lime and limestone for use in the paper industry with a production of 157,000 short tons; Missouri second with 151,000 short tons; and Pennsylvania third with 145,000 short tons. Paper making has also become an important industry in the South, and Tennessee and Alabama combined produced a total of 216,700 short tons of limestone for use in this industry.

In the soda process of preparing chemical pulp an important reuse of lime has been developed. The soda liquor, which is separated from the pulp, is concentrated and evaporated to dryness, and the ash is leached for its soda content. It becomes carbonated during the process and is converted into caustic soda ready for reuse by treating it with lime. The reaction is as follows: $Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$. The calcium carbonate settles out as a sludge, which is calcined into lime and is then available for reuse. At the West Virginia Pulp & Paper Co. plant, Charleston, S. C., the sludge is filtered, washed, and filtered again. The filter cake is then calcined in a 170-foot rotary kiln. As lime is lost in the pulp process, the filter cake made of the calcium carbonate sludge must be supplemented by the addition of limestone. The process has been so perfected that only about 25 pounds of make-up lime per ton of pulp is needed to replace that which is lost, whereas before the introduction of highly efficient kilns and other equipment 110 pounds per ton of pulp was required.

It is obvious from the above statement that the quantity of limestone sold to the paper industry is not a true measure of the quantity required per ton of pulp prepared, because a considerable quantity of the limestone is used repeatedly.

Refractories

Dolomite and high-magnesian limestone or their calcined products are used in lining metallurgical furnaces to resist the high temperatures and the corrosive action of basic slag. The raw stone is crushed, calcined, mixed with tar, and applied as a monolithic lining, or it may be shaped into bricks which are fired and used in the same manner as other refractory brick. Stone for this use is reported to the Bureau of Mines in two forms. Part is sold by the quarrying company to the manufacturer and is reported as raw stone; part is both quarried and dead-burned by the manufacturer and

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is reported as finished product. The foregoing historical tables show the amount of stone sold in both forms. Dead-burned material is used most commonly, although raw stone is employed for repair work. The Bureau of Mines has no data available showing a separation between the amount of raw stone and dead-burned material used.

Production of refractory stone is governed largely by steel output. With recent increased activity in steel plants, the production of limestone for refractory purposes reached an all-time high of over 2 million tons in 1939. Sales of raw stone were reported by 14 companies operating 17 plants in the following States: California, 1; Idaho, 1; Indiana, 2; Massachusetts, 1; Michigan, 1; Nevada, 1; New York, 1; Ohio, 5; Pennsylvania, 3; and West Virginia, 1.

Eleven companies representing 14 plants reported production of dead-burned dolomite in 1939, as follows: Alabama, 1; Illinois, 2; Missouri, 1; Ohio, 7; Pennsylvania, 2; and West Virginia, 1.

In 1939 over 45 percent of refractory sales were from Ohio. Pennsylvania and West Virginia are next in order.

Sugar

Lime is an indispensable material in the manufacture of beet and cane sugar. Its function is to precipitate impurities from the juices or syrup or to precipitate the sugar from impure solutions. Only high-calcium limestone, containing about 97 percent calcium carbonate and free from impurities that would impart a taste, is desired. Limestone is used in refining beet sugar by the carbonization process. The limestone is burned to lime, and both the lime and carbon dioxide gas are used. Because carbon dioxide as well as lime is necessary to beet-sugar refining, the raw stone is burned at the refinery. For every pound of beet sugar produced, a little more than half a pound of limestone is used in the manufacturing process. Cane-sugar refining companies buy burned lime because carbon dioxide is not necessary in the refining process.

The reuse of lime is also being employed in the sugar-refining industry. The Steffen process of refining sugar requires finely powdered quicklime, which precipitates sucrose from an aqueous solution of beet molassas. After the reaction is complete, the addition of carbon dioxide converts the lime into calcium carbonate, which precipitates and is removed by filtering. Filter cake is recalcined less extensively in the sugar than in the paper industry, but recently a continuous process has been perfected whereby recalcination probably will become a more important factor.

The States producing the greatest amount of limestone for use in sugar manufacture in 1939 were Michigan, Wyoming, and California, which together supplied about 60 percent of the total. Other large producing States were, in order of importance: Colorado, Montana, Nevada, Utah, Iowa, Idaho, Nebraska, and Illinois. A small tonnage was reported in Oregon. Ohio and Wisconsin are the only large beet-sugar producing States that did not report limestone production for use in the refining process.

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Small tonnages of lime for use in sugar refining were reported from Alabama, Arkansas, California, Florida, Illinois, Missouri, Pennsylvania, Tennessee, Texas, and West Virginia. Limestone burned and sold as lime constituted in 1939 approximately 4 percent of all the stone used in processing sugar.

Whiting

The Bureau of Mines considers whiting as divisible into three classes: Limestone and marble whiting, consisting of finely pulverized limestone (or crystalline limestone) of a quality suitable for use as a filler or pigment; chalk whiting, a material prepared from chalk; and precipitated whiting, material prepared as a precipitate from some soluble calcium salt or from a milk of lime suspension that has been recarbonated.

Very few deposits of true chalk suitable for the manufacture of whiting have been exploited in the United States. Consequently, during the World War when imports of chalk from England, France, and Denmark were curtailed, substitutes of domestic origin, which had not been produced extensively before, were used. After the war the use of limestone and marble as substitutes for whiting became increasingly important, and production rose accordingly.

Production of ground limestone and marble has recently been reported to the Bureau of Mines by 28 quarry companies in the following States: Alabama, California, Connecticut, Georgia, Illinois, Massachusetts, Michigan, Missouri, Nebraska, New Jersey, New York, Ohio, Pennsylvania, and Tennessee. Pennsylvania and Ohio together produced approximately 35 percent of the total stone used for whiting uses, with California closely following.

According to recent reports to the Bureau of Mines from producers, ground limestone is employed as a filler in or a constituent of the following commodities: Graphite, kalsomine, linoleum, paint, pigments, paper, polishing and buffing compounds, pottery, putty, rubber, sealing wax, soap, targets, tile, and wallboard. A number of additional uses have been mentioned in literature, but no sales to such industries have been reported to the Bureau of Mines. Separate tonnages for the various uses are not available because some quarry operators who sell ground limestone do not know how it is finally used.

APPLICATIONS EMPLOYING MODERATE TONNAGES

Fertilizer Filler

The use of limestone as a fertilizer filler has increased greatly in the past 5 years. Before 1935 only a few thousand tons of limestone were reported for this use, but from 1935 to 1939 the production has ranged from approximately 39,000 short tons to 116,000 tons. The filler adds weight to and reduces the caking of fertilizers, and also serves as a soil conditioner. Both dolomite and high-calcium limestone are satisfactory for this use.

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Filter Beds

Limestone and dolomite serve as hosts for organisms that purify sewage in sewage disposal works. The stone used is subjected to severe conditions with respect to both mechanical weathering (freezing and thawing) and to solution. Stone carefully screened and free from dust, fine stone, and dirt is essential for sewage filter beds. Impurities such as clay, pyrite, shale, ocher, marcasite, and chert are usually undesirable.

Production of limestone for filter beds has been reported recently from Georgia, Illinois, Maryland, New York, Ohio, Oklahoma, Pennsylvania, Texas, Virginia, and Wisconsin. Texas alone produced two-thirds of the total United States output, which amounted to 105,850 short tons in 1939.

Magnesia

Large quantities of dolomite are consumed annually for the manufacture of basic magnesium carbonate (also called technical carbonate, block magnesia, and magnesia alba), which finds its greatest outlet in the manufacture of pipe and boiler covering and general heat insulation. In the past 20 years the production of dolomite for this purpose has ranged between 32,050 (1921 production) and 126,260 (1936 production) short tons. Seven companies reported production of dolomite for this use in 1939 from California, Ohio, Pennsylvania, and Wisconsin. Virtually pure dolomite is used in Pennsylvania, where over 80 percent of the total United States output is produced.

A small quantity of lime from Wisconsin and Pennsylvania is also sold to magnesia works.

Mineral Food

Calcium is important to the success of livestock farming, because it serves as a bone builder, is necessary in the proper functioning of the nervous system, and also acts as a neutralizer in the digestive tract. According to the Kansas State Agricultural College, one-tenth pound of limestone should be consumed each day per head of livestock. A satisfactory limestone for stock food should contain at least 95 percent calcium carbonate, no fluorine, and very little magnesium. The stone must be ground almost as fine as wheat flour, which explains the high average price a ton ($3 to $5).

Production of limestone for mineral food was so small that before 1925 separate figures were not given in the Bureau of Mines reports. However, from 1925 to 1939, production has increased from 6,080 to 68,580 short tons annually. Over 80 percent of all the limestone produced for mineral food is from the Middle West (Missouri, Ohio, Nebraska, and Iowa, in order of tonnage produced).

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LIME IN MISCELLANEOUS PROCESSING INDUSTRIES

Lime is sold to the chemical industries for a number of uses, not included under limestone. The largest of these is lime used in water purification or softening. This use, which is steadily increasing, required 251,193 short tons of lime in 1939. According to the National Lime Association, the advantages of lime in hard water are: (1) The water is clarified and softened; (2) the corrosion of iron pipes is prevented, thus eliminating "red water" trouble; (3) the efficiency of sedimentation is increased, because better coagulation is brought about; (4) iron, objectionable gases, and coloration are removed; (5) filtration is made more efficient and economical; and (6) the water can be completely sterilized when lime is used in quantity adequate to kill the intestinal and pathogenic bacteria. Either quicklime or hydrated lime of high calcium content may be used.

The leather industry consumes 50,000 to 70,000 short tons of lime annually in dehairing or depilation of hides. Both quicklime and hydrated lime containing 85 percent or more calcium hydroxide may be used. However, in making Morocco leather high-magnesium lime is employed.

Between 40,000 to 50,000 short tons of lime is consumed each year in the preparation of insecticides, fungicides, and disinfectants. Following is a list of the more important of them.

Calcium arsenate	London purple
Lead arsenate	Calcium sulfide
Lime-sulfur	Barium sulfide-lime mixture
Dry sulfur-lime	Calcium permanganate
Bordeaux mixture	Lime cresol
Clorpicrin	Lime-nicotine
Bleaching powder	Whitewash
Lime tar	

The following products and processes consume from a few hundred to approximately 30,000 short tons of lime annually: Acid neutralization; alcohol; asphalts and other bituminous materials; bleach liquid and powder (exclusive of bleach for paper manufacture); sand-lime brick; slag brick; bromine; chromates and bichromates; coke and gas (gas purification and plant byproducts); food products (creameries and dairies, gelatin, phosphate baking powders); glue; grease (lubricating); petroleum refining; retarder; salt refining; sewage and trade-wastes treatment; starfish control; textiles; tobacco; and wood distillation.

Thus the production of limestone and its calcination product, lime, is an important industry in spite of the commonplace occurrence of the raw material. The uses of both limestone and lime should expand as new processes are developed. Producers should give constant consideration to methods of treatment or selection that will improve their product for special uses insofar as this is feasible under market conditions. Limestone and lime are low-cost commodities that are likely to replace other materials wherever substitution is possible.

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